



Consommation
et Corporations Canada

Consumer and
Corporate Affairs Canada

Bureau des brevets

Patent Office

Ottawa, Canada
K1A 0C9

(21) (A1)	2,050,518
(22)	1991/09/04
(43)	1992/03/08

5,049,0/42

(51) INTL.CL.⁵ C08G-016/04; D06M-015/39

(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Aromatic Condensation Products

(72) Walz, Klaus - Germany (Federal Republic of) ;
Hendricks, Udo - Germany (Federal Republic of) ;
Ehlert, Hans-Albert - Germany (Federal Republic of) ;
Lesszinsky, Fritz - Germany (Federal Republic of) ;

(73) Bayer Aktiengesellschaft - Germany (Federal Republic of)
;

(30) (DE) P 40 28 534.0 1990/09/07

(57) 10 Claims

Notice: The specification contained herein as filed

Canada

CCA 3254 (10-89) 41

Aromatic condensation products

A b s t r a c t

The aromatic formaldehyde condensation products, which are substantially colourless and water-soluble and contain sulphonate and/or carboxylate groups, are obtainable by adding agents which have a reducing action during and/or after the condensation reaction, and are suitable for the treatment of textiles and leather.

Le A 27 854-US

Aromatic Condensation Products

Background of the Invention

The present invention relates to aromatic formaldehyde condensation products which are substantially colourless and water-soluble and contain sulphonate and/or carboxylate groups.

Water-soluble aromatic formaldehyde condensation products are known per se (see Ullmanns Enzyklopädie der technischen Chemie (Ullmann's encyclopaedia of technical chemistry) Volume 16 (1979), pages 140 et seq.) and can be prepared by the processes reported on there or by processes such as are described, for example, in Houben-Weyl: "Methoden der organischen Chemie" (Methods of organic chemistry) Volume 14/2, pages 263-292, G. Thieme Verlag Stuttgart (1963), or in German Offenlegungsschrift 1,960,616 and German Offenlegungsschrift 1,961,369.

However, the known aromatic formaldehyde condensation products have a strong intrinsic colour, which has proved very disadvantageous, particularly when these products are used in the textile field.

Summary of the Invention

The present invention relates to aromatic formaldehyde condensation products which are substantially colourless and water-soluble and contain sulphonate and/or carboxylate groups and which are characterised in that they are obtainable by adding agents having a reducing action, with the exception of sodium sulphite, sodium bisulphite and sodium pyrosulphite, during and/or after the condensation reaction, and to the use thereof for the treatment of textiles and leather.

Compared with the known aromatic formaldehyde condensation products, the products prepared in accordance with the invention are distinguished by a drastically reduced intrinsic colour. In addition, the tendency to yellowing, with and without the action of light, of textiles treated with these products is substantially reduced, whether they are used in the dyebath or as an after-treatment.

Detailed Description of the Invention

Water-soluble condensation products containing sulphor and/or carboxylate groups are to be understood as meaning oligomeric or polymeric products which are obtainable by the condensation with formaldehyde of one or more aromatic and, if appropriate, non-aromatic compounds capable of undergoing condensation, in which at least one of the aromatic compounds must contain at least one sulphonate and/or carboxylate group, or in which the sulphonate groups are introduced during or after the condensation reaction.

Examples of suitable aromatic compounds capable of undergoing condensation are benzene and naphthalene derivatives each of which is substituted by C₁-C₄-alkyl and/or hydroxyl and/or cycloalkyl and/or C₁-C₄-alkoxy and/or C₁-C₄-hydroxyalkoxy and/or aroxy and/or aralkoxy and/or carboxyl and/or carboalkoxy and/or sulphonate and/or arylsulphonyl radicals.

The following may be mentioned as examples: xylene, mesitylene, phenol, cresols, xylenols, butylphenol, cyclohexylphenol, anisole, phenoxyethanol, phenoxypropanol, phenoxyacetic acid, phenolsulphonic acid, anisole-sulphonic acid, diphenyl ether, ditolyl ether,

5 dihydroxydiphenyl sulphone, 2,2-bis-4-hydroxyphenylpropane, 4-hydroxydiphenyl sulphone, bis-(hydroxyethoxyphenyl) sulphone, salicylic acid, 4-hydroxybenzoic acid, naphthalene, naphthols, isobutylnaphthalene, naphtholsulphonic acids, naphthyl methyl ether, biphenylsulphonic acid, sulphonated dihydroxydiphenyl sulphone and diphenyl-ether-sulphonic acid.

10 In addition to the aromatic compounds capable of undergoing condensation, it is also possible, in addition, to employ, for the preparation of the water-soluble condensation products, non-aromatic compounds capable of condensation, such as, for example, urea, thiourea, ethyleneurea, ethylenethiourea and/or melamine.

15 The introduction of sulphonate groups during or after the condensation reaction can be effected in a customary manner, for example by reaction with sulphur trioxide, sulphuric acid or chlorosulphonic acid, or by reaction with formaldehyde and sulphites or bisulphites.

20 Water-soluble condensation products which are particularly preferred are those prepared by the joint condensation of dihydroxydiphenyl sulphone and phenolsulphonic acid and/or biphenylsulphonic acid and/or dihydroxybiphenylsulphonic acid and/or ditolyl-ether-sulphonic acid and/or naphthalenesulphonic acids and/or hydroxybenzoic acids
25 with formaldehyde. Other condensation products which are particularly preferred are obtained by the condensation of dihydroxydiphenyl sulphone with formaldehyde and

alkali metal sulphites or bisulphites, and of dihydroxydiphenyl-sulphone-sulphonic acids with formaldehyde.

5 Customary reducing agents which can be employed in chemical reactions can be used as the agents having a reducing action. The following may be mentioned as examples: hydrogen, activated hydrogen, metal hydrides, such as sodium hydride, sodium borohydride or lithium aluminium hydride, sulphur compounds having a reducing action, such
10 as sulphites, with the exception of sodium sulphite, bisulphites, with the exception of sodium bisulphite, hydrosulphites, pyrosulphites, with the exception of sodium pyrosulphite, dithionites, thiosulphates, sulphyoxylates, hydroxymethanesulphinates, sulphinates or
15 thiourea dioxide, phosphorus compounds having a reducing action, such as phosphorous acid or hypophosphorous acid or salts thereof, and also organic reducing agents, such as glucose, gluconic acid or hydroxyacetone.

20 The amounts of agents having a reducing action to be employed are 0.1 to 20 %, preferably 0.5 to 10 % (relative to the finished condensation product).

In a preferred embodiment one or more complex-formers are added before, during and/or after the condensation reaction. Customary complex-forming agents, such as are
25 described, for example, in C.H. Fischer-Bobsin: Internationales Lexikon, Textilveredlung und Grenzgebiete (International dictionary of textile finishing and

related fields), 4th edition 1975, A. Laumannsche Verlagsbuchhandlung, Dülmen, page 918 et seq., can be used as such complex-formers.

5 Examples of suitable complex-formers are: tartaric acid, citric acid, nitrilotriacetic acid, ethylenediaminetetraacetic acid and polyaminopolycarboxylic acids or alkali metal or ammonium salts thereof, condensed phosphates, such as, for example, sodium tripolyphosphate or metaphosphate, and also phosphonic acids, in particular
10 phosphonic acids or salts thereof containing carboxyl groups and/or hydroxyl groups and/or amino groups, such as, for example, phosphonosuccinic acid, 2-phosphono-1,2,4-butanetricarboxylic acid, aminomethanephosphonic acid, amino-trismethylenephosphonic acid, hydroxymethanephosphonic acid, hydroxyethanephosphonic acid, hydroxyethanediphosphonic acid, hydroxyethylaminomethylenephosphonic acid or diethylenetriamine-pentamethylenephosphonic acid or alkali metal or ammonium salts thereof.

20 The complex-formers can be employed in amounts of 0.1 - 10 %, preferably 0.5 - 5 %, relative to the condensation products. Preferred preparations are obtained if the aromatic condensation products are prepared in the presence of

25 0.5 - 10 % of a reducing agent, in particular alkali metal or ammonium hydroxymethanesulphinates or dithionites or thiourea dioxide, and

0.5 - 5 % of a complex-former, in particular nitrilo-
triacetic acid, ethylenediaminetetraacetic
acid, hydroxyethanediphosphonic acid and
aminomethylenephosphonic acids,

5 or if these agents are added to the finished condensation
products in aqueous solution and, if appropriate, the
mixture is heated at 30 to 100°C for a short time.

In addition to the components mentioned in the preferred
embodiment, the preparations according to the invention
10 can also contain other constituents, such as solvents,
solubilisers, anionic or nonionic polymers, emulsifiers,
anti-foaming agents and others.

The condensation products and preparations prepared in
accordance with the invention can be employed in various
15 industrial fields, such as, for example, as dispersing
agents for water-insoluble solids, for example dyestuff
or pigments, resists and agents for improving fastness in
textile dyeing, tanning agents or in the stain-repellent
finishing of textile materials composed of, for example,
20 synthetic polyamide fibres.

Example 1

134 parts of phenolsulphonic acid, 50 parts of water,
250 parts of 4,4'-dihydroxydiphenyl sulphone and 45 parts
of 45 % strength sodium hydroxide solution are mixed in
25 a pressure vessel and 90 parts of 30 % strength

formaldehyde solution are then added. After the vessel has been closed it is heated with stirring to 120°C and condensation is carried out at this temperature for 5 hours. After cooling to approx. 80 - 90°C, 300 parts of water are added, whereupon a dark brown viscous solution A is formed.

338 parts of water, approx. 20 parts of sodium hydroxide solution (45 % strength) and 15 parts of thiourea dioxide are added to 626 parts of this solution A, and the mixture is stirred for 30 minutes at 20 - 30°C and is then heated slowly to 90°C. Approx. 1000 parts of a light-coloured solution having a colour number of 7 - 10 are obtained.

A solution, prepared for comparison, of the condensation product at the same concentration was prepared by diluting solution A with 373 parts of water. The solution obtained has a colour number of 500 - 600.

Example 2

27 parts of ethylene glycol, 1.5 parts of sodium hydroxide solution (45 % strength), 8.2 parts of thiourea dioxide and 120 parts of water are added to a condensation product, prepared in accordance with Example 1, of 112 parts of technical dihydroxydiphenyl sulphone, 41 parts of technical phenolsulphonic acid (65 % strength solution in water), 40 parts of sodium hydroxide solution (45 % strength), 46 parts of formaldehyde (30 % strength)

and 150 parts of water, and the mixture is heated at 90 - 95°C for 1 hour with stirring. Approx. 540 parts of a pale brown solution (colour number 30) are obtained.

5 A solution of the same concentration, but without after-treatment with thiourea dioxide, has a colour number of 900 - 1000.

Example 3

10 125 parts of dihydroxydiphenyl sulphone, 25 parts of sodium sulphite, 18 parts of sodium hydroxide solution (45 % strength), 56 parts of formaldehyde solution (30 % strength) and 257 parts of water are mixed in a pressure vessel. After the vessel has been closed it is heated at 120 - 125°C with stirring and condensation is carried out for 24 hours.

15 3 parts of sodium hydroxymethanesulphinate, 2 parts of nitrilotriacetic acid and 67 parts of water are added to 127 parts of the solution obtained above, and the mixture is stirred at room temperature for 12 hours. Approx. 200 parts of a nearly colourless solution are obtained
20 (colour number 4 - 7).

A solution having a colour number of 300 - 400 is obtained by diluting, to the same content of active compound, the solution obtained in the preparation of the condensation product.

Example 4

5 8.4 parts of sodium hydroxide solution (45 % strength),
6 parts of sodium hydroxymethanesulphinate, 152 parts of
water and 2.4 parts of hydroxyethane-1,1-diphosphonic
acid are added to 209 parts of the solution A prepared in
accordance with Example 1, and the mixture is stirred for
1 hour at room temperature. It is then heated at 80 -
90°C for 30 minutes. Approx. 375 parts of a nearly
colourless solution are obtained (colour number 5 - 10).

10 Example 5

15 82.8 parts of 98 % strength sulphuric acid are added to
117 parts of diphenyl ether and the mixture is stirred at
130 to 140°C for 4 hours. After it has cooled to 50 to
60°C, 180 parts of water, 160 parts of technical dihy-
droxydiphenyl sulphone and 106 parts of a 30 % strength
aqueous solution of formaldehyde are added. The mixture
is heated to 90 to 95°C and is stirred at this tempera-
ture for 6 hours. After it has cooled to 60 to 70°C,
20 400 parts of water and 180 parts of 25 % strength sodium
hydroxide solution are added. Clarification by filtration
gives a solution having a solids content of 32 %, a
viscosity of 8.4 mPa.s at 20°C and an iodine colour
number of 250 to 300.

25 100 g of the solution are heated with 1.5 parts of sodium
dithionite and 0.6 part of hydroxyethane-1,1-diphosphonic
acid at 90 to 95°C for 30 minutes under an atmosphere of

nitrogen. A solution having a colour number of 4 to 7 is obtained.

Example 6

5 80 parts of 98 % strength sulphuric acid are added at room temperature to 68.8 parts of anisole, and the mixture is then stirred at 90 to 95°C for 30 minutes. 60 parts of water, 115 parts of technical dihydroxydiphenyl sulphone and 78 parts of 30 % strength aqueous formaldehyde solution are added, and the mixture is heated slowly to 100 to 105°C and is stirred for 3 hours at this temperature. The supernatant solution is poured off from the resin formed, and 400 parts of water and 260 parts of 20 % strength sodium hydroxide solution are added to the resin, and the mixture is stirred at 60 to 15 70°C until solution takes place. Clarification by filtration gives a solution having a solids content of 28.5 %, a viscosity of 5.3 mPa.s at 20°C and an iodine colour number of 160 to 200.

20 100 g of the solution are heated with 3 parts of sodium dithionite and 0.6 part of hydroxyethane-1,1-diphosphonic acid at 90 to 95°C for 30 minutes under an atmosphere of nitrogen. A solution having a colour number of 7 is obtained.

What is claimed is:

- 5 1. A substantially colourless, water-soluble aromatic formaldehyde condensation product containing sulphonate and/or carboxylate groups, which is obtainable by adding agents having a reducing action, with the exception of sodium sulphite, sodium bisulphite and sodium pyrosulphite, during and/or after the condensation reaction of formaldehyde with one or more aromatic and, if appropriate, non-aromatic compounds capable of undergoing condensation.
- 10 2. The aromatic formaldehyde condensation product of claim 1, wherein the aromatic compounds capable of undergoing condensation which are used are benzene and naphthalene derivatives each of which is substituted by C₁-C₄-alkyl, and/or hydroxyl, and/or cycloalkyl, and/or C₁-C₄-alkoxy, and/or C₁-C₄-hydroxy-alkoxy, and/or aroxy, and/or aralkoxy, and/or carboxyl, and/or carboalkoxy, and/or sulphonate, and/or arylsulphonyl radicals.
- 15 3. The aromatic formaldehyde condensation product of claim 1, wherein besides the aromatic compounds capable of undergoing condensation, non-aromatic compounds capable of undergoing condensation are also employed in addition.
- 20 4. The aromatic formaldehyde condensation product of claim 1, wherein the non-aromatic compounds capable of undergoing condensation are urea, thiourea, ethyleneurea, ethylenethiourea and/or melamine.
- 25 5. The aromatic formaldehyde condensation product of claim 1, wherein the water-soluble condensation product is one which is obtained by the joint condensation of dihydroxydiphenyl sulphone and phenolsulphonic acid and/or biphenylsulphonic acid and/or dihydroxybiphenylsulphonic acid and/or ditolyl-ether-sulphonic acid and/or naphthalenesulphonic acids and/or hydroxybenzoic acids with formaldehyde or by the condensation of dihydroxydiphenyl sulphone with formaldehyde and alkali metal bisulphites, and of dihydroxydiphenylsulphone-sulphonic acid with formaldehyde.
- 30 6. The aromatic formaldehyde condensation product of claim 1, wherein the agents having a reducing action which are used are hydrogen, activated hydrogen, metal hydrides, sulphites, bisulphites, hydrosulphites, pyrosulphites, dithionites,
- 35

thiosulphates, sulphonylates, hydroxymethanesulphinates, sulphinates or thiourea dioxide, or phosphorous acid or hypophosphorous acid or salts thereof, and also organic reducing agents.

7. A dressing containing an aromatic formaldehyde condensation product of claim 1, wherein the aromatic condensation product is prepared in the presence of

0.5 - 10 % of a reducing agent, in particular alkali metal or ammonium hydroxymethanesulphinates or dithionites, or thiourea dioxide, and

0.5 - 5 % of a complex-former, in particular nitrilotriacetic acid, ethylenediaminetetraacetic acid, hydroxyethanediphosphonic acid and aminomethylenephosphonic acids,

or these agents are added to the finished condensation product in aqueous solution and, if appropriate, the mixture is heated at 30 to 100°C for a short time.

8. The aromatic formaldehyde condensation product of claim 1, wherein the water-soluble condensation product is obtained by the condensation of dihydroxy-diphenyl sulphone and phenolsulphonic acid.

9. The aromatic formaldehyde condensation product of claim 1, wherein thiourea dioxide or alkali metal or ammoniumsulphinates or dithionites are used as the agent having a reducing action.

10. A process for the treatment of a textile or leather wherein an aromatic formaldehyde condensation product of claim 1 is employed as the treatment agent.